

MECHANICAL PROPERTIES OF EUROPIUM-DOPED
SODIUM CHLORIDE

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PREFACE

This study is concerned with the analysis of the effect of the divalent europium ion on the mechanical properties of a specific alkali chloride, NaCl. The primary objective is to determine the strengthening of the NaCl single crystals as a function of the concentration of divalent europium and as a function of the quenching temperature. Several models of hardening are compared to the data which has been obtained.

The author wishes to express her appreciation to her major adviser, Dr. J. J. Martin, not only for his guidance and assistance throughout this study, but also for his patience and advice on scholastic curriculum.

In addition, special heart-felt gratitude is expressed to my parents, Andrew H. and Valeria F., for their long years of understanding, encouragement, and numerous sacrifices.

TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION.	1
II. THEORY.	3
III. EXPERIMENTAL PROCEDURE.	10
Crystal Development.	10
Optical Analysis	12
Flow Stress Measurements	14
Quenching.	15
IV. RESULTS AND DISCUSSION.	18
V. CONCLUSIONS	23
SELECTED BIBLIOGRAPHY	24

LIST OF FIGURES

Figure	Page
1. Oklahoma State University Crystal Puller	11
2. Optical Absorption Curves for Crystals	13
3. Stress-Strain Curve for a Typical Eu^{2+} Doped NaCl Crystal. .	16
4. Resolved Flow Stress Versus Concentration for Various Crystals	19
5. Resolved Flow Stress Versus Concentration for Crystals Prepared in Various Methods	20
6. Resolved Flow Stress Versus Quenching Temperature for NaCl: Eu^{2+} Crystals	22

CHAPTER I

INTRODUCTION

Within the last ten years, alkali halides have been of particular interest as possible window materials for high power CO_2 lasers. A criterion for laser window application is low optical absorption in the infra-red range, due to the fact that a CO_2 laser operates at a wavelength of 10.6 microns. Within these years, there have been numerous experiments conducted in the area of alkaline earth divalent impurities such as Ca^{2+} , Sr^{2+} , and Ba^{2+} and the effect upon the properties of polar crystals such as NaCl, KCl, and KBr. These studies include ionic conductivity, dielectric loss, optical absorption, electron spin resonance, and mechanical properties.

This work was initiated to study the effect of impurity doping on the mechanical property of NaCl. The dopant used was Eu^{2+} . Undoped single crystals of NaCl have rather low mechanical strength, but the powdered crystalline form is relatively inexpensive. Thus, if the crystal could be made stronger, it could be of interest.

There exist different mechanical effects that the defect has on the crystalline solid. Fleischer (1), Snoek (2), and Suzuki (3) have developed models for the interaction of various defects with dislocations which results in strengthening of the crystal. Fleischer discussed tetragonal defects such as those introduced by ionizing radiation or by impurity-vacancy pairs. Snoek proposed long-range ordering of dipoles

in the stress field of moving dislocations. Suzuki employed the model of hardening due to segregation of solute atoms at a stacking fault by chemical interaction.

While much work has been accomplished on alkali halides, there remains work to be done on the mechanical strength of NaCl. The low mechanical strength of NaCl may be significantly altered by introduction of defects either through irradiation or by divalent impurities. The F center is one such type of defect. Sibley and Sonder (4), Nadeau (5,6), and Lerma and Agulló-López (7,8) have shown that the halogen interstitial produced during F center formation by irradiation causes significant hardening in alkali halides. Using impurity ions as dopants also causes strengthening as shown by Sill and Martin (9), Pratt et al. (10), and Chin et al. (11). Furthermore, NaCl:Eu^{2+} is a convenient system in which to observe the flow stress versus the concentration, due to the fact that the Eu^{2+} ion is optically active in the u.v. range. Hernandez et al. (12) directly related the absorption coefficient to the concentration.

There has been considerable work accomplished with various alkali chlorides and bromides doped with divalent ions. The increase in strength observed will be compared to not only the various theories, but also to previous experimental data completed by Chin et al. (11), Pratt et al. (10), Sibley et al. (13), and Sill and Martin (9).

CHAPTER II

THEORY

Doping alkali chloride single crystals with divalent ions results in strengthening of the crystal. This effect has been observed in KCl:Eu by Sill and Martin (9), in NaCl:Ca²⁺ by Newey (14), and in KCl:Sr²⁺ by Sibley et al. (15) to name a few. Moreover, the optical properties of the crystal can be related to the mechanical properties. For instance, Hernandez et al. (12) determined a non-destructive method for determining the concentration of Eu²⁺ in alkali chlorides. This concentration can be directly related to the flow stress as seen in Fleischer's work. This is only one example of the relationships that occurs between spectroscopy techniques and mechanical properties.

Divalent europium has a 4f⁷ electronic configuration. In conformity with Hund's rule, the ground state is ⁸S_{7/2}. Röhrig (16) determined from the EPR spectroscopy for europium-doped alkali halides, that the divalent europium ion at room temperature is associated with a defect in a <100> direction. The incorporation of a divalent europium ion in place of the monovalent sodium ion requires either the presence of an anion impurity of valence -2 or a cation vacancy in the lattice to form pairs of the type Eu²⁺ plus a sodium vacancy in order to retain neutrality. It has been established using the electron paramagnetic resonance technique (17,18,19) that the Eu²⁺ doping of alkali chloride single crystals resulted in the formation of an impurity-alkali vacancy

pair. The divalent impurities and associated cation vacancies may be distributed as individual defects independent of one another, as impurity-vacancy pairs, or in aggregates. For the paired defect, the cation vacancies may assume the nearest, second-nearest, or third-nearest neighboring positions with respect to the divalent impurity. The EPR spectra broaden with temperature due to thermally-activated motion of the vacancy about the Eu^{2+} ion (16,17). Furthermore, the orthorhombic sites exhibit a long-term instability when the crystals are stored at room temperature. The EPR spectra are returned to original state by low temperature anneal as reported by Röhrig (16).

Röhrig (16) assumed the most likely interpretation of the non-cubic crystal field is a vacancy at the nearest alkali ion site. Upon distortion of the lattice around this europium-vacancy defect, the crystal field is lowered to orthorhombic symmetry for new crystals. Aguilar et al. (17) further explored the orthorhombic symmetry related to the Eu^{2+} spectra.

The optical spectra are accounted for by the strong crystal field split 5d electron having a Coulomb interaction with the $4f^6$ core (20). Shen (21) assumed Hund's rule is applicable for the optically active excited states of the $4f^6 5d$ configuration where this state is 8P_J with J going from 5/2 to 9/2. The low energy band is attributed to the transition from the ground state to the t_{2g} component. The high energy band is due to the transition to the e_g component.

Reisfeld and Glasner (22) found the optical properties of the phosphors were characteristic of divalent europium in their work with europic chloride and bromide. The fluorescence peaks of these compounds are located at 430 mμ and 424 mμ. As reported by Hernandez et al.

(12,20), the Eu^{2+} ion produces two broad optical absorption bands at room temperature for alkali chlorides, alkali bromides, and KI. In all cases the low energy band exhibits a characteristic multi-step like structure in the 320 nm to 400 nm range. Pascual et al. (23) assumed that the location of the low energy band is independent of concentration of the Pb^{2+} impurity in NaCl, KCl, and KBr. The relative heights of the high- and low-energy bands are noticeably different between as-grown crystals and quenched crystals. The peak of the high energy band shifts to longer wavelengths in as-grown KCl. Furthermore, he ascribes the high energy band to tetragonal symmetry, which is the symmetry of the next-nearest neighbor configuration of the defect, while the low energy emission band is due to trigonal symmetry.

In alkali halides the lattice contains a large strain along the axis of the divalent ion and its associated positive ion vacancy. During flow stress measurements, large number of dislocations are forced through the crystal sample under the impetus of the external force. These dislocations move along sampling the resistance presented by lattice defects. Fleischer's (1) theory of crystalline strengthening is in terms of the tetragonal lattice distortion around the divalent ion and its associated cation vacancy. To calculate the hardening due to the tetragonal defect, Fleischer made several assumptions to simplify computations. First, depending upon the separation, the force on a dislocation from a short range defect must decrease rapidly. That is, the stress due to the dislocation is assumed constant over the volume of the defect. Also the strain due to the defect is constant over a small volume near the defect and negligible elsewhere. The defect concentration is also assumed to be small so that defect-defect interactions can

be neglected. Thus the dislocation moving on its slip plane is affected only by the defects on the slip plane. Now assume that a defect exerts a maximum force, F_m , on a dislocation. The force per unit length on the dislocation is F_m/l where l is the average spacing of defects on the plane. The increase in stress, τ , to move the dislocation is

$$\tau = F_m/bl$$

where b is the slip or Burger's vector of the dislocation. The atomic concentration, C , is given by

$$C = A/l^2$$

where A is the cross-sectional area of the defect. The flow stress becomes

$$\tau = F_m C^{1/2}/bA^{1/2}$$

The yield point may be related to the locking of dislocations by solute atoms, where dislocations are torn away from the impurity atmospheres by the applied stress. Fleischer assumed the interaction to be of a short range nature. He then related the F_m to the shear modulus G and geometrical factors. The flow stress reduces to

$$\tau = (G/n)C^{1/2}$$

Fleischer calculated n , a number depicting the hardening effectiveness of a particular type of defect, to be 10 and 100 for an interstitial defect and a divacancy defect, respectively. Fleischer (1) categorized defects as causing gradual hardening or rapid hardening due to their effect on the resistance to motion and multiplication of dislocations

in the crystalline solid. Thus for the gradual hardening, n is 100. This type of defect produces a symmetric lattice distortion and does not interact with screw dislocations. For rapid hardening, where n is 10, a non-symmetric distortion is produced, which interacts strongly with screw dislocations.

This square root dependence is found in NaCl:Ca^{2+} only for slow cooled crystals in which the Ca^{2+} vacancy pairs are in an aggregated state. For quenched samples, Chang (24) proposed that a Snoek effect occurs, whereby a long range ordering of dipoles in the stress field of moving dislocation occurs. The yield stress in quenched NaCl:Ca^{2+} is linearly dependent on the concentration of the dopant ion. The Snoek effect is the process whereby, at temperatures where the interstitials can reorient, the applied stress will cause a redistribution in the population of different lattice sites. This locks the dislocation. According to Schoeck and Seeger (25), the Snoek effect is accomplished by atomic rearrangement between neighboring lattice sites.

Pratt et al. (10) proposed a treatment of the Snoek effect that considers the dislocation-defect interaction to be a long range ordering of the dipoles in the stress field of moving dislocations. In the stress field, the twelve impurity-vacancy pair orientations are no longer equivalent in energy. The dipoles assume the orientation of the lowest energy state, provided that they are allowed to move. To lower the energy of the dislocation along a stationary dislocation, the dipoles will be distributed in the stress field among the twelve possible orientations according to a Boltzmann distribution. If the distribution were frozen and the dislocation moved out of this ordered atmosphere into a random distribution, the energy difference of the two states must be

supplied by the applied stress. If the dipoles have enough time to reorient while the dislocation passes them, the dislocation will appear to drag an ordered atmosphere along with it. The flow stress is predicted to be proportional to the concentration of dipoles.

Chang and Graham (24) state that the defect cluster in Ca^{2+} doped NaCl is essentially tetragonal in the $\langle 100 \rangle$ directions. They further state, that for this defect, reorientation of the pairs with respect to the stress fields of a moving dislocation takes place by one or two nearest-neighbor jumps of the sodium ion vacancy about the impurity. The strengthening is due to a cloud dragging mechanism similar to the Snoek effect. For defect clusters whose reorientation depends upon coordinated movements of both the impurity ions and the cation vacancies, strengthening takes place by the mechanism proposed by Fleischer.

Chin et al. (11) determined that the yield strength of air cooled samples is dependent on dopant concentration only and independent of species involved. Furthermore, they found that upon aging of air cooled samples, some decreased in strength while others increased. It was found that aging resulted in agglomeration of dipoles into higher order complexes and precipitates. Extensive studies of dipole aggregation using dielectric loss measurements by Dryden and others (26,27,28) suggest that dipoles aggregate to form trimers, that is, three dipoles in a cluster.

Yacamán (29) stated that the Suzuki affect in NaCl:Eu^{2+} is similar to that of NaCl:Ca^{2+} in that the precipitates initially form as platelets located on the $[111]$ and $[310]$ planes. At a later stage of precipitation, CaCl_2 crystallites appeared in the matrix. Suzuki (3,30,31) found that for short periods of aging only $[310]$ platelets predominated

while after a month [111] platelets became detectable. Yacamán observed cleavage steps and indicated that these were due to interaction with precipitates which were present before cleavage.

CHAPTER III

EXPERIMENTAL PROCEDURE

Crystal Development

Single crystals of pure sodium chloride and europium doped sodium chloride were pulled using the Kyropoulous-Czochralski technique. The single crystal growth phase of this work was to provide similarly produced single crystals to insure that the boules were of the same quality. These boules were grown from Harshaw cleaved seeds. The reagent grade crystalline powder produced by Mallinckrodt was placed in a Coors alumina crucible. Europium dichloride was added in measured amounts depending on the desired concentration of the dopant. This mixture along with the seed on the pull rod was placed under vacuum for several hours. The furnace temperature was increased to 450°C for approximately fourteen hours under a vacuum produced by a diffusion pump.

The water-cooled vacuum/argon chamber contained a cylindrical internally mounted graphite heater and a circular bottom heater. This latter heater was later changed to a series of graphite radiation shields. The crystal puller is depicted in Figure 1. Furthermore, during the single crystal growth process, a controlled atmosphere of approximately -660 mm/vac of gettered argon was maintained in the growth chamber during growth and cool down of each boule. Pull rates of 0.6 cm/hr or less were used.

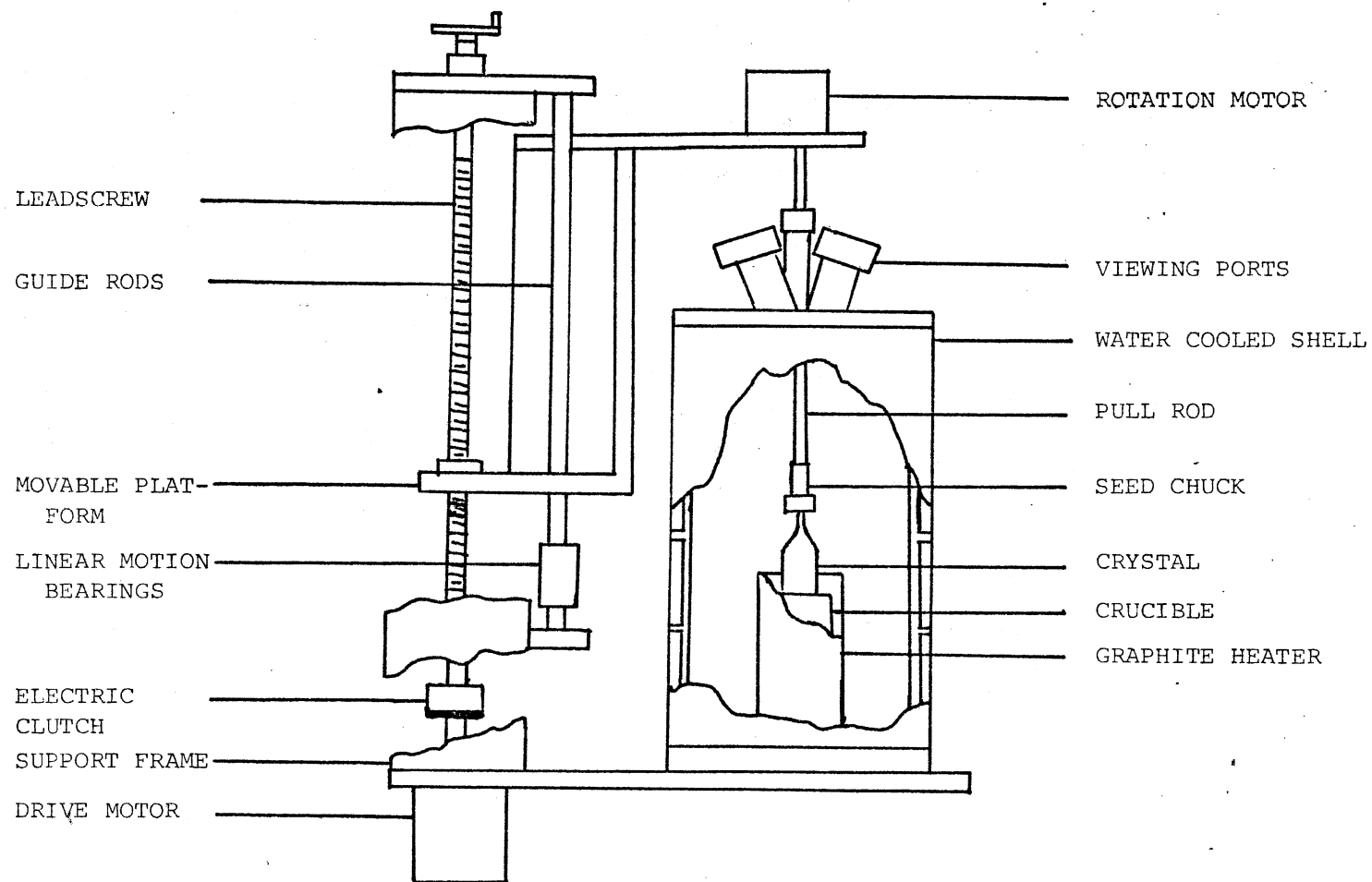


Figure 1. Oklahoma State University Crystal Puller

The europium dichloride used as a dopant was produced by a hydrogen reduction process similar to that used by Johnson and Mackenzie (32). However, gettered argon was allowed to flow through the fused quartz combustion tube for thirty minutes before the introduction of the graphite boat that contained the anhydrous europium chloride from the Research Organic/Inorganic Chemical Corporation to purge the tube of air. The temperature was raised from 200°C to 700°C in increments of no more than 100°C per hour. The maximum temperature was maintained for two hours before allowing the apparatus to slowly cool down. During this process hydrogen was allowed to flow periodically after 600°C was reached and steadily at 700°C. The gettered argon flow was continuously maintained throughout the process. After cool down, the europium dichloride was removed from the graphite boat and placed in small glass vials until usage.

Optical Analysis

Due to the fact that one looks at the resolved flow stress as a function of dopant concentration, it became mandatory to employ a technique whereby each individual sample from the single crystal could be non-destructively measured for Eu^{2+} concentration in order that the same sample could be used for compression tests. These optical test samples were cleaved perpendicular to the growth axis in order to maintain a uniform distribution of Eu^{2+} for that sample.

It has been determined that the Eu^{2+} ion produces two strong optical absorption bands in alkali chlorides by both Mehra (33) and Hernandez et al. (12). These bands are located in the ultraviolet region between 200 nm and 400 nm as seen in Figure 2. At room tempera-

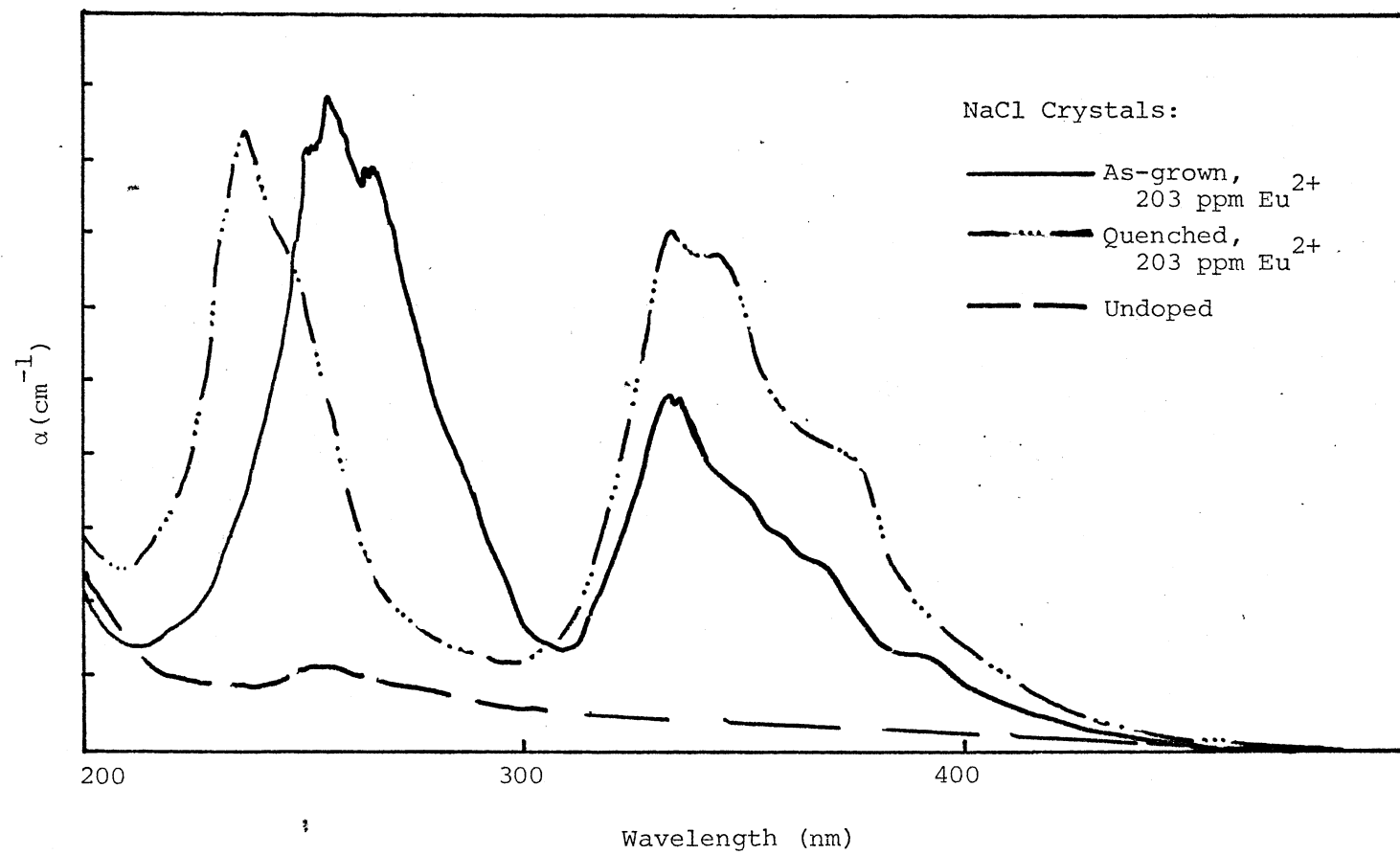


Figure 2. Optical Absorption Curves for Crystals

ture the 330 nm band has a characteristic multistep-like structure, while the 243 nm band is unstructured under certain conditions. Thus the 243 nm absorption band peak may be routinely used in the non-destructive determination of dopant concentration. This spectrum is obtained with a Cary 14 spectrophotometer.

Now for aged crystals, a different optical absorption spectrum is obtained as shown in the comparison in Figure 2. This compares a crystal that has been quenched after approximately twenty-four hours to an aged crystal. The position of the high energy band shifts from 243 nm to 260 nm. Furthermore, the 260 nm band now contains resolvable structure. Then for these peaks, the concentration may be determined using the method described by Hernandez, et al. (12). For the new or quenched crystal whose high energy band is at 243 nm,

$$N(\text{p.p.m.}) = 12\alpha(\text{cm}^{-1})$$

where N is the Eu^{2+} concentration in atomic parts per million and α is the absorption coefficient. Similarly, for the aged crystal with a high energy band at 260 nm,

$$N(\text{p.p.m.}) = 11\alpha(\text{cm}^{-1}) .$$

Flow Stress Measurements

The flow stress in most cases is a direct measure of the resistance to the motion of fresh dislocations through the crystal along the primary slip directions. This flow stress was measured under uniaxial compression for numerous samples from each single crystal giving a wide range of Eu^{2+} concentration. From this data the flow stress can be compared to the dopant concentration. Furthermore, to insure a homogeneous

Eu^{2+} concentration, plates ranging from 1.0 mm to 2.0 mm in thickness were cleaved perpendicular to the growth axis from the single crystal boules. The actual measurement of the Eu^{2+} concentration involved calculating the absorption coefficient α from the optical absorption curve as determined on the Cary 14 spectrophotometer for each optical sample.

The compression measured by the Instron was along the $\langle 100 \rangle$. The chart recording produced was a record of the applied force versus time. These samples for the compression tests were cleaved from the optical samples, where a typical compression sample measured 1.0 mm x 1.5 mm x 5.0 mm. Due to the configuration of the compression sample, end effects could be neglected. These samples were compressed with an Instron crosshead speed of 0.05 cm/min corresponding to a strain rate of 10^{-4} sec^{-1} . A typical stress-strain curve for NaCl:Eu is shown in Figure 3. The engineering flow stress, τ_e , was considered to be designated by the intersection of the tangent lines of the Hooke's law region to the first plastic portion of the stress-strain curve.

Due to the fact that flow stress measures the resistance to motion along the primary slip direction, the resolved flow stress, τ_r , was calculated. Since the primary slip direction is in the $\langle 110 \rangle$ for NaCl (4), the resolved flow stress is one half of the engineering flow stress. That is, τ_r is the component of the flow stress that is parallel to the primary slip direction.

Quenching

Upon annealing the sample, slow cooling results in the precipitation of impurities from the solid solution. Such was found to be the case with the Eu^{2+} doping of NaCl. This type of single crystal was

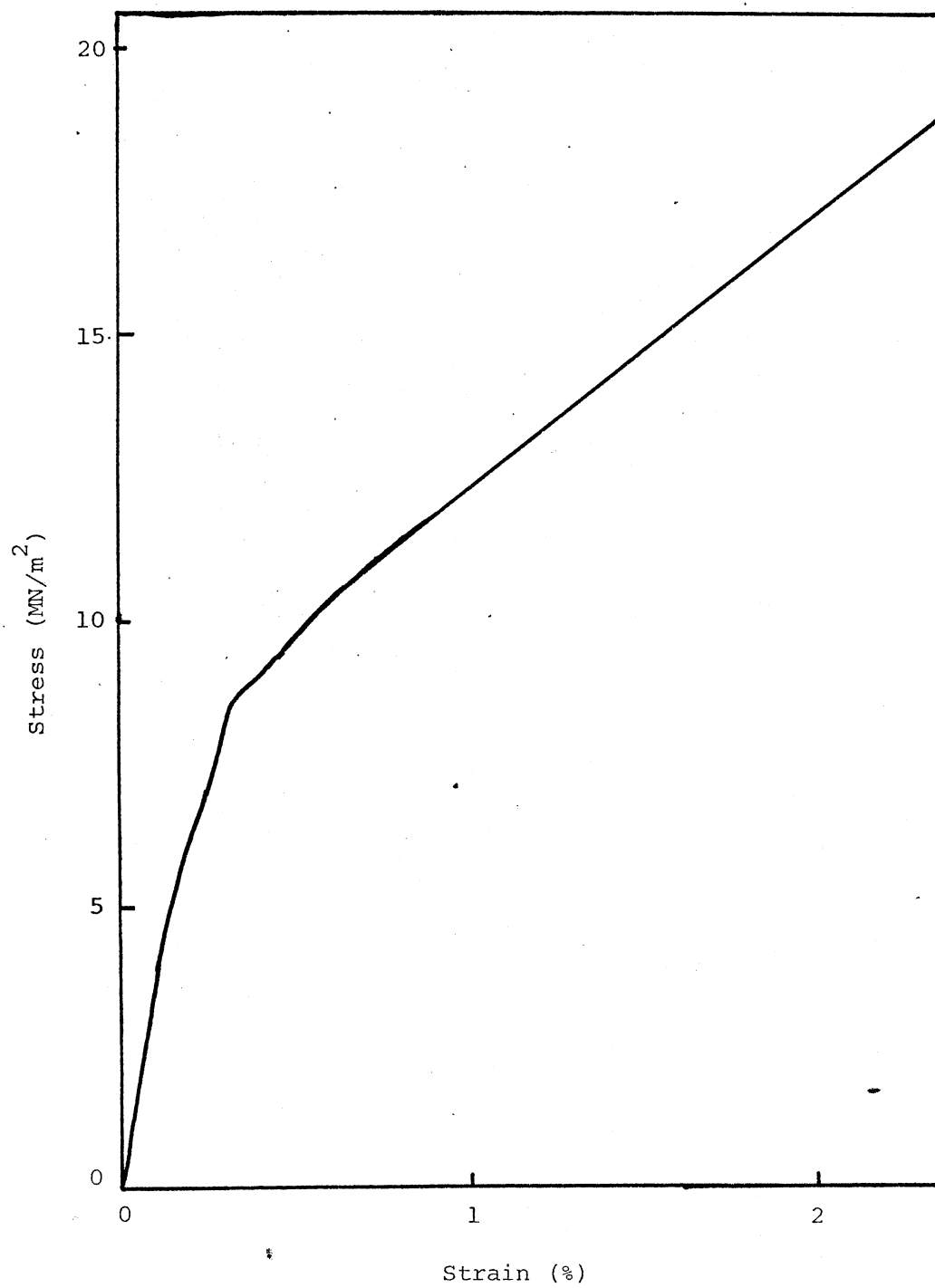


Figure 3. Stress-Strain Curve for a Typical Eu^{2+} Doped NaCl Crystal

found to contain precipitates after a few weeks as compared to KCl:Eu which took up to six or more months to form precipitates as indicated by Sill and Martin (5). Thus, it now became necessary not only to quench the optical samples from around 800°K to find the concentration as previously mentioned, but also to place the sample in a comparable state to a freshly grown crystal.

With rapid quenching the equilibrium defect present at the quench temperature, T_q , is retained. The rate of quenching may be varied by choice of the quench medium. However, the quench rate can increase the strain-induced effect in the mechanical properties. Thus various quench mediums were investigated. Samples were then quenched on a metal block. To reduce strain-induced effects on the mechanical properties of the doped samples, these specimens were observed under a polarizer-analyzer. The strained portions of the sample were removed before any compression tests were run.

CHAPTER IV

RESULTS AND DISCUSSION

The Eu^{2+} ion was found to be useful as a strengthening agent for NaCl single crystals. The increase in flow stress was shown to be a function of the square root of the concentration for as-grown crystals. Figure 4 shows the flow stress versus Eu^{2+} concentration for samples cleaved from as-grown crystals. The flow stress does not increase linearly with the concentration. This result is in agreement with the results for $\text{KCl}:\text{Sr}^{2+}$ by Sibley (13) which shows a $C^{\frac{1}{2}}$ dependence. This relationship agrees with the model of hardening proposed by Fleischer (1). Since Fleischer's theory assumed that the interactions are short ranged in nature, one may decide that the interactions are indeed short ranged. Furthermore, if the dipoles have combined to form larger complexes, then the vacancies would no longer be free to orient themselves. The dependency would not be linear with concentration in this case.

Due to the large scattering of data for quenched samples, later samples were examined under crossed polarizers to determine strained areas which were then cleaved from the samples before flow stress measurements were determined. The data for quenched samples also shows that the Eu^{2+} ion is an effective hardening agent, but it is less effective than the Ca^{2+} ion. As seen in Figure 5, the flow stress of the as-grown crystal is greater than the quenched sample to approximately 300 ppm of Eu^{2+} . Note that the flow stress is linear with respect to

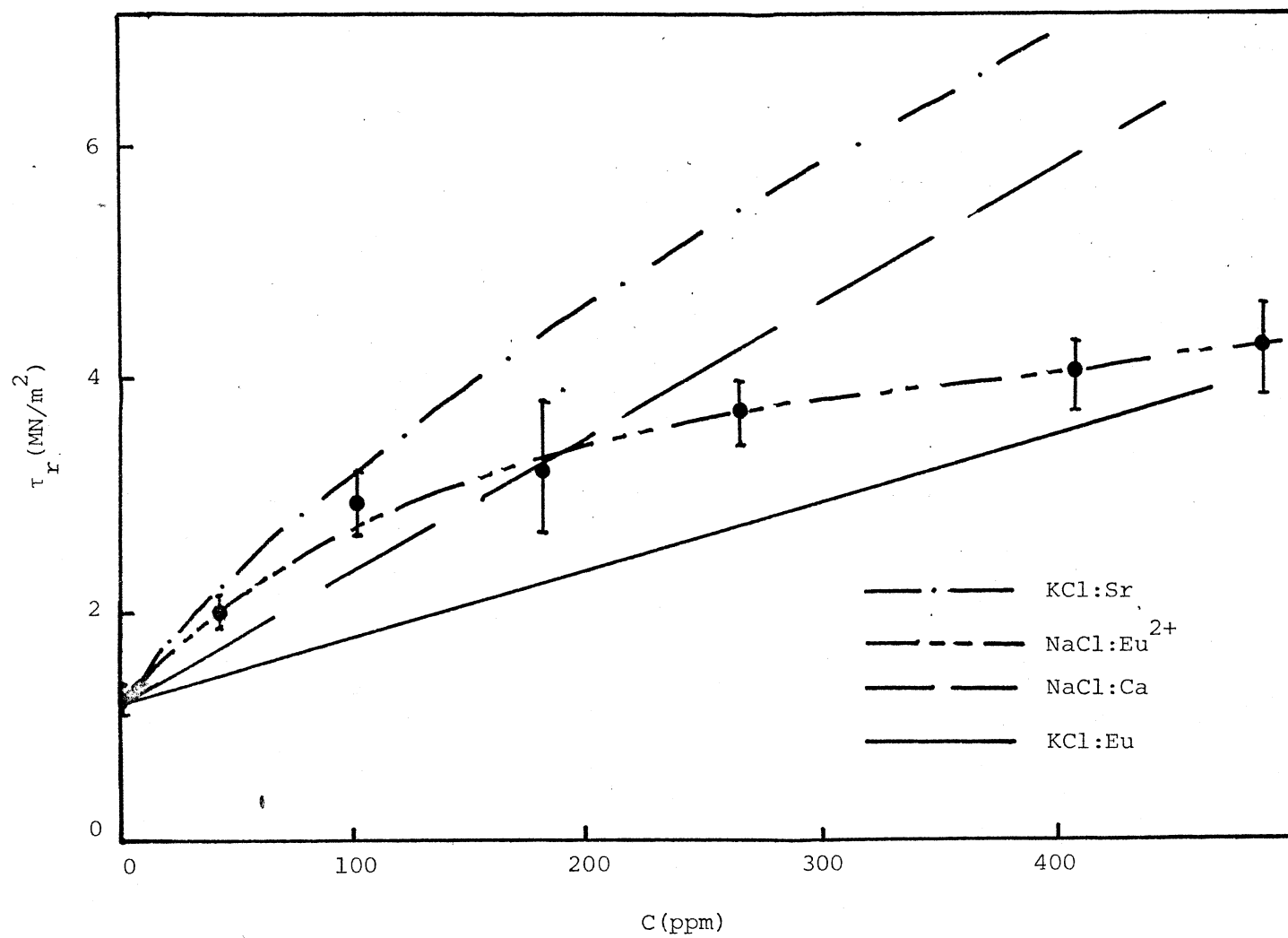


Figure 4. Resolved Flow Stress Versus Concentration for Various Crystals

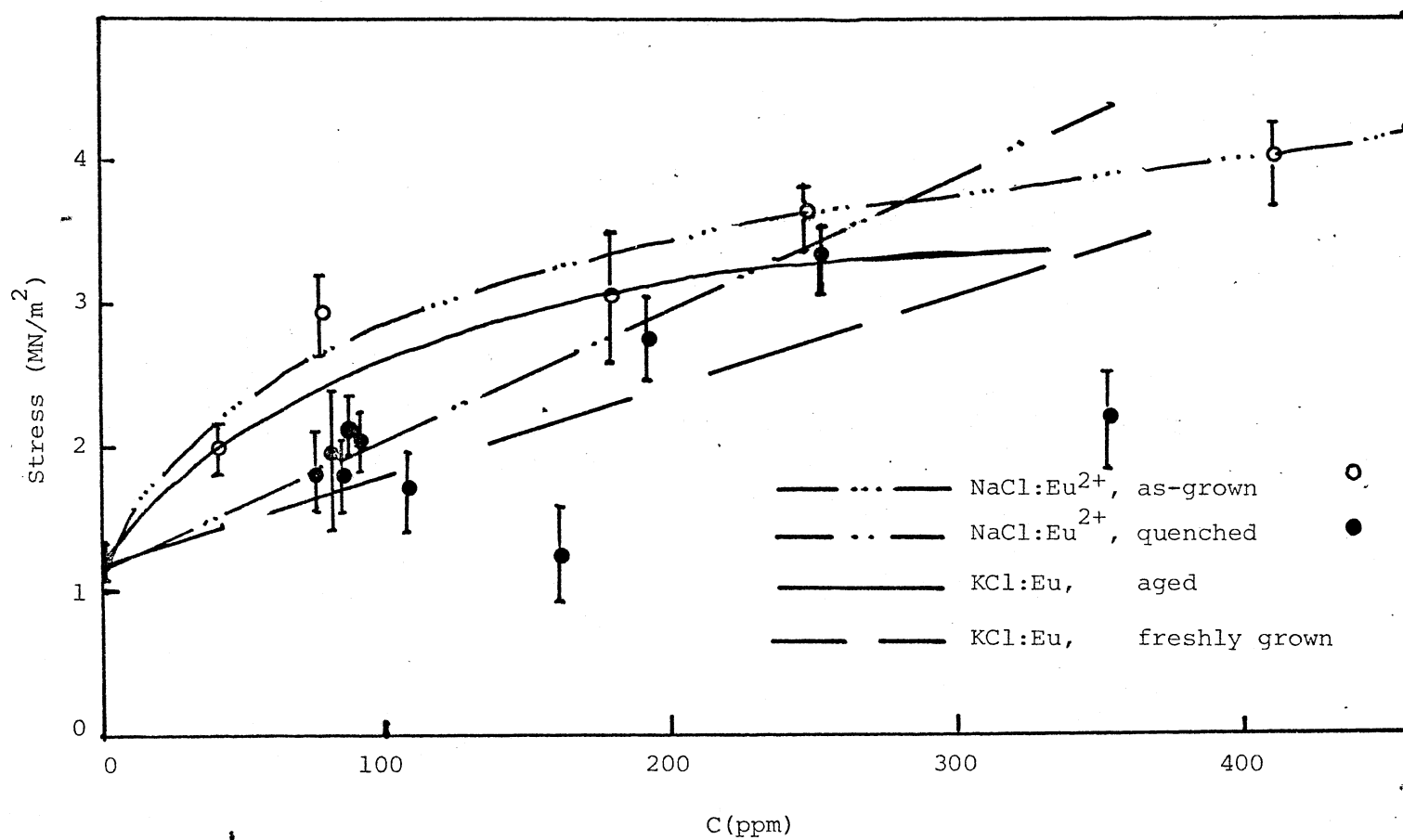


Figure 5. Resolved Flow Stress Versus Concentration for Crystals Prepared in Various Methods

concentration. This occurrence no longer agrees with Fleischer's model for hardening. For quenched crystals, the method of hardening follows the Snoek effect discussed by Pratt et al. (10) that there is a long range ordering of the divalent impurity-vacancy pairs when in the stress field of a moving dislocation. This implies that the majority of the defects are single dipoles rather than large aggregates. It can also be seen in Figure 5 that NaCl:Eu^{2+} is mechanically stronger than KCl:Eu . However, it is evident that NaCl:Ca^{2+} and KCl:Sr^{2+} have a larger flow stress than either NaCl:Eu^{2+} or KCl:Eu .

It is also of interest to look at the resolved flow stress versus the quenching temperature as seen in Figure 6. There exists a definite decrease in resolved flow stress between 200°C and 400°C . It should also be noted that the flow stress follows a non-linear dependence on concentration for samples quenched at low temperatures. Once the quenching temperature is around 400°C , the flow stress begins to vary linearly with the concentration.

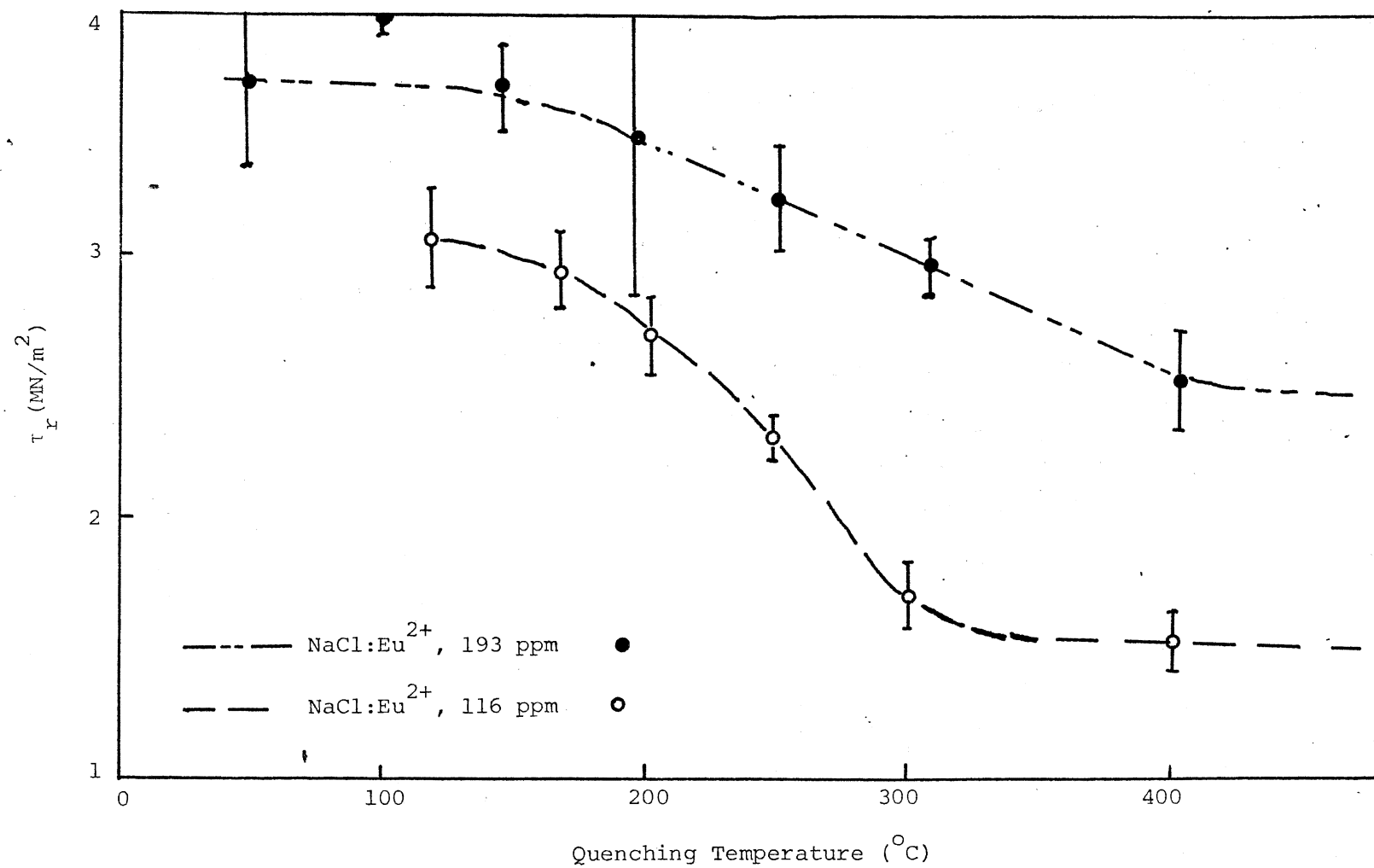


Figure 6. Resolved Flow Stress Versus Quenching Temperature for $\text{NaCl}:\text{Eu}^{2+}$ Crystals

CHAPTER V

CONCLUSIONS

The quenched samples of NaCl:Eu^{2+} have a flow stress that is linear with concentration of Eu^{2+} . This linear dependence on the concentration was also found in NaCl:Ca^{2+} by Pratt et al. (10) and Chang (24). This dependence was also observed by Sill and Martin (9) in KCl:Eu . It appears, that for NaCl:Eu^{2+} , a Snoek effect occurs whereby a long range ordering of dipoles takes place in the stress field of a moving dislocation. This implies that the majority of defects are not in large aggregations, but rather they are single dipoles, a Eu^{2+} impurity ion plus a cation vacancy, that are spread throughout the sample when it has been quenched from approximately 450°C .

SELECTED BIBLIOGRAPHY

1. Fleischer, R. L. "Solution Hardening by Tetragonal Distortions: Application to Irradiation Hardening in F.C.C. Crystals." ACTA Metallurgica, 10 (1962), pp. 835-842.
2. Snoek, J. "Effect of Small Quantities of Carbon and Nitrogen on the Elastic and Plastic Properties of Iron." Physica, 8 (1941), pp. 711-733.
3. Miyake, S. and K. Suzuki. "X-ray Studies on the Structures of Solid Solutions NaCl-CaCl₂." Journal of the Physical Society of Japan, 9 (1954), pp. 702-712.
4. Sibley, W. A. and E. Sonder. "Hardening of KCl by Electron and Gamma Irradiation." Journal of Applied Physics, 34 (1963), No. 8, pp. 2366-2370.
5. Nadeau, J. S. "Hardening of Potassium Chloride by Color Centers." Journal of Applied Physics, 34 (1963), No. 8, pp. 2248-2253.
6. Nadeau, J. S. "Radiation Hardening in Alkali-Halide Crystals." Journal of Applied Physics, 35 (1964), No. 4, pp. 1248-1255.
7. Lerma, I. S., and F. Agulló-López. "Temperature Dependence of Irradiation Hardening in NaCl." Journal of Applied Physics, 41 (1970), No. 11, pp. 4628-4631.
8. Lerma, I. S. and F. Agulló-López. "Different Hardening Behavior of Low and High Dose γ -Irradiated NaCl Single Crystals." ACTA Metallurgica, 17 (1969), pp. 1459-1465.
9. Sill, E. L. and J. J. Martin. "Flow Stress of Eu Doped KCl." Mat. Res. Bull., 12 (1977), pp. 127-132.
10. Pratt, P. L., R. Chang and C. W. A. Newey. "Effect of Divalent Metal Impurity Distribution, Quenching Rate, and Annealing Temperature on Flow Stress in Ionic Crystals." Applied Physics Letters, 3 (1963), No. 5, pp. 83-85.
11. Chin, G. Y., L. G. Van Uitert, M. L. Green, G. J. Zydzik, and T. YL Kometani. "Strengthening of Alkali Halides by Divalent Ion Additions." Journal of the American Ceramic Society, 56 (1973), No. 7, pp. 369-372.

12. Hernandez, A., W. K. Cory and J. Rubio O. "A Non-Destructive Method for Determining the Eu^{2+} Concentration in the Alkali Chlorides." Japanese Journal of Applied Physics, 18 (1979), No. 3, pp. 533-538.
13. Sibley, W. A., C. T. Butler, J. R. Hopkins, J. J. Martin, J. A. Miller, Annual Technical Report No. 1, AFCRL-TR-73-0342, 30 April 1973.
14. Newey, C. W. A. "Strengthening of NaCl Crystals by Additions of Ca^{2+} ." Trans. Brit. Ceram. Soc., 62 (1963), pp. 739-751.
15. Sibley, W. A., C. T. Butler, J. R. Hopkins, and J. J. Martin, Semi-Annual Technical Report No. 2, AFCRL-TR-74-0156, 31 October 1973.
16. Röhrig, R. "Electron Spin Resonance of Eu^{++} in Alkali Halides." Physics Letters, 16 (1965), No. 1, pp. 20-21.
17. Aguilar, G. S., E. Munoz P. and H. Murrieta S. "EPR Investigations of Eu^{2+} in Orthorhombic Sites of NaCl." The Journal of Chemical Physics, 60 (1974), No. 12, pp. 4665-4669.
18. Nair, P. G., K. V. Lingam and B. Venkataraman. "Electron Spin Resonance of Eu^{2+} in KCl." J. Phys. Chem. Solids, 29 (1968), pp. 2183-2191.
19. Rubio, J. O., E. Munoz P. and G. Aguilar S. "Electron Paramagnetic Resonance of Eu^{2+} in Orthorhombic Sites in RbCl Single Crystals." J. Chem. Phys., 61 (1974) No. 12, pp. 5273-5274.
20. Private Communications with Hernandez, J. A., W. K. Cory and J. O. Rubio. "Optical Investigation of Divalent Europium in the Alkali Chlorides and Bromides."
21. Shen, Y. R. "Faraday Rotation of Rare-Earth Ions. I. Theory." Physical Review, 133 (1964), No. 2A, pp. A511-A515.
22. Reisfeld, R. and A. Glasner. "Absorption and Fluorescence Spectra of Eu^{2+} in Alkali Halide Crystals." Journal of the Optical Society of America, 54 (1964), No. 3, pp. 331-333.
23. Pascual, J. L., L. Arizmendi, F. Jaque and F. Agulló-López. "Luminescence Spectra of Lead-Doped NaCl, KCl and KBr." Journal of Luminescence, 17 (1978), pp. 325-343.
24. Chang, R. and L. J. Graham. "The Elastic Interaction Between Dislocations and Defects Associated with Calcium Impurities in Sodium Chloride." ACTA Cryst., 17 (1964), pp. 795-799.
25. Schoeck, G. and A. Seeger. "The Flow Stress of Iron and Its Dependence on Impurities." ACTA Metallurgica, 7 (1959), pp. 469-477.

26. Cook, J. S. and J. S. Dryden. "An Investigation of the Aggregation of Divalent Cationic Impurities in Alkali Halides by Dielectric Absorption." Proc. Phys. Soc., 80 (1962), pp. 479-488.
27. Dryden, J. S. "The Aggregation of Divalent Impurities and Their Associated Cation Vacancies in Alkali Halides." J. Phys. Soc. Japan, Suppl. III, 18 (1965), pp. 129-133.
28. Dryden, J. S. and G. G. Harvey. "Dielectric and Optical Properties of Lead-Activated Sodium and Potassium Chloride Crystals." J. Phys. C. (Solid State), 2 (1969), pp. 603-618.
29. Yacamán, M. J. and G. A. Bassett. "Gold Decoration of Precipitates in Doped Alkali-Halide Surfaces." Journal of Applied Physics, 47 (1976), No. 6, pp. 2313-2315.
30. Suzuki, K. "X-ray Studies on the Structures of Solid Solutions NaCl-CaCl₂." Journal of the Physical Society of Japan, 10 (1955), No. 9, pp. 794-804.
31. Suzuki, K. "X-ray Studies on the Structures of Solid Solutions NaCl-CaCl₂." Journal of the Physical Society of Japan, 13 (1958), No. 2, pp. 179-186.
32. Johnson, K. E. and J. R. Mackenzie. "Anhydrous Chlorides of Some Rare Earths." J. Inorg. Nucl. Chem., 32 (1970), pp. 43-48.
33. Mehra, A. K. "Optical Absorption of Eu²⁺-Doped KCl." Journal of the Optical Society of America, 58 (1968), pp. 853.

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